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THE COMPUTATION OF THE PARTIAL VOLUMES OF THE COMPONENTS IN SOLUTION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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THE COMPUTATION OF THE PARTIAL VOLUMES OF THE COMPONENTS IN SOLUTION

INTRODUCTION

The partial volumes of the components in solution are important and are frequently used in thermodynamic calculations. A number of methods have been developed for calculating these quantities [1] but the calculation of the partial volumes from the corresponding apparent volumes of the solution are convenient [2, 3] and appear to enjoy special favor because of a possible theoretical basis [4]. This is because of the empirical relation of Masson [5], who found that the apparent volume of the solute of electrolytes in aqueous solutions is a linear function of the square root of the volume concentration. Though this relation has found some theoretical confirmation for dilute solutions, it has often been found inadequate because the relation does not always extend to concentrated solutions. Modifications of Masson's relation are, therefore, frequently necessary, so that the essential problem of finding the partial volumes from a related quantity which can always be expressed analytically in the same form has not been achieved. It is not inappropriate, therefore, to describe the method given below for calculating the partial volumes since it is generally applicable to both aqueous and non-aqueous solutions of both electrolytes and non-electrolytes.

We have previously [6] derived the equation

$$v_s^{(P)} = x_1 c^\alpha (v_w^{(P)} - b) + b x_1 + x_2 \psi_2^{(P)} \quad (1)$$

where $v_s^{(P)}$, $v_w^{(P)}$ and $\psi_2^{(P)}$ are, respectively, the specific volumes at pressure P , of the solution, water and the volume of the solute in solution. Also x_1 and x_2 are the weight fractions of water and solute and α , the concentration of the solute, will be defined as either x_2 , the weight fraction of the solute, or by (x_2/v_s) , the volume concentration (we will distinguish this by α'); b is the constant in the equation

$$P_0 - P = a \log \left(\frac{v_w^{(P)} - b}{v_w^{(P_0)} - b} \right) \quad (2)$$

which represents the variation of volumes of water with pressure.

In this expression $v_w^{(P_0)}$ and $v_w^{(P)}$ are the specific volumes of water at the pressure P_0 and P , and the two parameters a and b may be determined by adapting the equation to the compressibility data of water.¹ Although equation (1), and hence equation (2), is expressed for water as solvent, the equations are generally applicable to both aqueous and non-aqueous solutions of electrolytes or non-electrolytes.

Equation (1) has been obtained by the combined use of equation (2), which is a variation of Tait's equation [4, 6 - 9] and Tammann's hypothesis, to the effect that water in solution is compressed by an ionized solute.

In particular, at atmospheric pressure, we will write for equation (1)

$$v_s = x_1 c^\alpha (v_w - b) + bx_1 + x_2 \psi_2 \quad (1')$$

where for convenience we have omitted the superscript which designates pressure; v_s , v_w and ψ_2 will be used to indicate, respectively, the volumes of the solution, pure water and the volume of the solute at atmospheric pressure. We will derive our equations for the partial volumes for atmospheric pressure, the results holding approximately at higher pressures.

In equation (1') only c and ψ_2 are unknown (after α is appropriately defined and the value of b selected) and these may be found by writing this equation for each concentration (using density data for the solutions at atmospheric pressure) and determining by the method of least squares their best values.²

¹The values of these parameters for water (and for a number of other solvents) have been determined with the initial pressure P_0 taken at atmospheric pressure; see Rosen [5]. b varies slowly as the pressure range is increased, but, as will be noted later, the value of b is not critical for our application.

²In reference [6] the parameters for a number of electrolytes in water were derived in this way from equation (1'). Equation (1) was then used (after appropriate provisions were made for determining $\psi_2^{(P)}$, the solute volumes at higher pressures) to compute the volumes of these salts in solution to 10 000 bars.

If we set

$$\psi_1 = c^\alpha (v_w - b) + b$$

then equation (1') becomes

$$v_s = x_1 \psi_1 + x_2 \psi_2$$

where ψ_1 is the specific volume of water in solution (whose values depend on the concentration) and where ψ_2 is the volume of the solute in solution and varies with pressure but is assumed to be constant for all concentrations. From the expression for ψ_1 in equation (3) it is evident that only a portion of the water, $v_w - b$, is compressed (since $c < 1$ for aqueous solutions of electrolytes). Thus, b is the relatively incompressible portion of the volume of water and, because its value is not critically determined by equation (2), neither is ψ_2 , the solute volume in equation (1'). In addition, it is evident that the choice between the two definitions of α (or others that may be used) would determine the values of ψ_1 and ψ_2 .³ However, the equations we will derive for the partial volumes, though different for either definition of the concentration used, give essentially the same numerical values for the partial volumes with different values for b and α .

EQUATIONS FOR PARTIAL VOLUMES

We rewrite equation (1')

$$v_s = x_1 c^\alpha (v_w - b) + bx_1 + x_2 \psi_2 + \delta,$$

where the δ is the difference between the observed and calculated volumes of the solution and is readily computed for each concentration once c and ψ_2 are found as previously indicated by the least squares method.

³For an interpretation of the volumes of the solute, ψ_2 , which result from equation (1') for a particular choice of α and b , see Rosen [9].

The specific partial volumes of the components in a solution are given by the expressions⁴

$$\bar{v}_1 = v_s - x_2 (dv_s/dx_2) \quad (5)$$

$$\bar{v}_2 = v_s + x_1 (dv_s/dx_2) \quad (5')$$

where the subscripts 1 and 2 refer to the solvent and solute, respectively.

Substituting equation (4) into these equations, we get the following relations for the partial volumes:

$$\bar{v}_1 - \psi_1 = -x_1 x_2 (v_w - b) (c^\alpha \ln c) + \Delta \bar{v}_1 \quad (6)$$

$$\bar{v}_2 - \psi_2 = x_1^2 (v_w - b) (c^\alpha \ln c) + \Delta \bar{v}_2 \quad (6')$$

and

$$\bar{v}_1 - \psi_1 = -x_1 (v_w - b) c^{\alpha'} \alpha' (\bar{v}_1/v_s) \ln c + \Delta \bar{v}_1 \quad (7)$$

$$\bar{v}_2 - \psi_2 = (x_1^2/x_2) (v_w - b) c^{\alpha'} \alpha' (\bar{v}_1/v_s) \ln c + \Delta \bar{v}_2 \quad (7')$$

where ψ_1 is given by equation (3) and the value of c corresponds to using for α and α' the concentrations x_2 and (x_2/v_s) . To these equations have been added the part resulting from the least square residuals, δ , and which we have designated by $\Delta \bar{v}_1$ and $\Delta \bar{v}_2$; so that by equations (5) and (5') can be written

$$\Delta \bar{v}_1 = \delta - x_2 (d\delta/dx_2) \quad (8)$$

$$\Delta \bar{v}_2 = \delta + x_1 (d\delta/dx_2) \quad (8')$$

The derivatives⁵ in equations (8) and (8') are most readily obtained by numerical differentiation from a table of divided differences (of equal or unequal intervals of x_2) of the δ 's as arguments of x_2 . In this table we are not limited to the arguments of x_2 used in fitting equation (1'). This has several advantages in both convenience and accuracy. In the first place, the exactness in determining the parameters of equation (1') is not important, nor is it necessary to use all the density data available in obtaining this fit if the deviation

⁴These define the partial volume per gram; the partial molal volume is obtained by multiplying these values by their molecular weight. Throughout this paper we use specific volumes instead of the corresponding molal volumes.

⁵ δ is of the order 1×10^{-4} (often, a fraction of this); however, $d\delta/dx_2$ is usually not negligible, especially at $x_2 = 0$.

curve is used.⁶ Secondly, as new or revised data for the solution is obtained, only the contributions to the partial volumes given by equations (8) and (8') need be recomputed.

When $x_2 = 0$, $\bar{v}_1 = v_w$, but equations (6') and (7') (which becomes indeterminate) quite readily give the equations

$$(\bar{v}_2)_{x_2=0} = \psi_2 + (v_w - b) (\ln c) + (d\delta/dx_2)_{x_2=0} = 0 \quad (9)$$

and

$$(\bar{v}_2)_{x_2=0} = \psi_2 + (v_w - b) (1/v_w) \ln c + (d\delta/dx_2)_{x_2=0} = 0 \quad (9')$$

for α and α' , respectively. At this concentration the partial volume is equal to the apparent volume and a stringent test for any interpolation equation is the limiting value obtained for this parameter.

For $x_2 = 1$, equations (6') and (7') give \bar{v}_2 , while equation (1') gives $v_s = \psi_2$. This limiting value for the partial volume has been identified as the hypothetical maximum value of the apparent volume and associated with it is a "critical disruptive volume" corresponding to the upper limit to the concentration of the solute in solution. For the alkali halides this comparison has been made with the limiting results derived from Masson's empirical relation on apparent volumes [4, 9].

As we have previously indicated, the equations we have derived for the partial volumes also hold at higher pressures. In these equations all the volumes are expressed for the required pressure while c , α , α' and b are held constant. $\psi_1(P)$ is given by equation (3), while $\psi_2(P)$ may be obtained by a method previously described [4, 6].

In Tables I through III are shown the partial volumes of the components of aqueous solutions of ammonium nitrate. These, computed by the equations developed here, are compared with the carefully determined values given by Adams and Gibson [10]. For the method they use in determining these partial volumes see footnotes to Table I. Except at $x_2 = 0$, these values agree almost exactly at all concentrations. From the results in these tables it would also appear

⁶This is not peculiar to equation (1') alone; it is generally true when a deviation curve is used. However, this fact is helpful here as equation (1') may be fitted by an approximate method more easily than by the exact least square method.

that our equations for the partial volumes of the components of the solution are not dependent on the value assumed for the parameter b , or whether the concentration of the solution is expressed by x_2 or x_2/v_s .

At $x_2 = 0$, our values for the partial volume of ammonium nitrate⁷ differ from the value given by Adams and Gibson (0.5932), but our results are approximately what would be obtained if their partial volumes for the higher concentrations were extrapolated to $x_2 = 0$ (0.5981).

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⁷These are 0.5976, 0.5975 and 0.5982 for the parameters shown in Tables I, II, III, respectively. The slope of our deviation curve at $x_2 = 0$ was computed from the data for 1, 5 and 10 percent solutions.

TABLE I. THE PARTIAL VOLUMES OF AMMONIUM NITRATE
AT 25°C COMPUTED BY EQUATION (6')^a

x_2	v_s^b	δ^c	$(\bar{v}_2)^c$	$\Delta\bar{v}_2^c$	\bar{v}_2 Eq. (6')	\bar{v}_2^d A & G	$10^4 \Delta^c$
0.00	1.00293	0.00000	0.60337	-0.00573	0.59764	0.5932	-44.4
0.15	0.94433	-0.00005	0.62011	0.00066	0.62077	0.6207	-0.7
0.30	0.88843	0.00001	0.63308	0.00015	0.63323	0.6332	-0.3
0.375	0.86138	0.00003	0.63829	0.00002	0.63831	0.6383	-0.1
0.45	0.83489	0.00001	0.64273	-0.00016	0.64257	0.6426	+0.3
0.525	0.80893	0.00000	0.64646	-0.00009	0.64637	0.6463	-0.7
0.55	0.80040	-0.00003	0.64755	-0.00014	0.64741	0.6474	-0.1

NOTES:

a. The constants used in equations (1') and (6') are:

$$b = 0.8591, c = 0.69215, \psi_2 = 0.6563, \alpha = x_2.$$

b. The data of Adams and Gibson [10].

c. The symbols used above are:

δ is the difference between the observed specific volume of solution and the value calculated by equation (1').

(\bar{v}_2) is used here to designate the partial volume calculated by equation (6') without the $\Delta\bar{v}_2$ term.

$\Delta\bar{v}_2$ is given by equation (8') and is the correction to the partial volume caused by the deviations δ .

Δ is the difference between the partial volumes found by Adams and Gibson and those computed by equation (6').

d. The partial volumes computed by Adams and Gibson [10]. They found the partial volumes by fitting two equations for the apparent volumes as functions of the weight fraction of salt and by using a deviation curve.

TABLE II. THE PARTIAL VOLUMES OF WATER IN
AMMONIUM NITRATE SOLUTION AT 25°C
COMPUTED BY EQUATION (7)^a

x_2	v_s^b	δ^c	$(\bar{v}_1)^c$	$\Delta\bar{v}_1^c$	\bar{v}_1 Eq. (7)	\bar{v}_1^d A&G	$10^4 \Delta^c$
0.00	1.00293	0.00000	1.00293	0.00000	1.00293	1.00293	0
0.15	0.94433	-0.00020	1.00183	-0.00031	1.00152	1.00145	-0.7
0.30	0.88843	0.00001	0.99818	-0.00041	0.99777	0.99782	0.5
0.375	0.86138	0.00008	0.99521	0.00002	0.99523	0.99523	0
0.45	0.83489	0.00003	0.99150	0.00071	0.99221	0.99222	0.1
0.525	0.80893	-0.00015	0.98692	0.00171	0.98863	0.98868	0.5

NOTES:

a. The constants used in equations (1') and (7) are:

$$b = 0.8591, c = 0.67362, \psi_2 = 0.66313, \alpha' = (x_2/v_s)$$

b. The data of Adams and Gibson [10].

c. Refer to the footnotes in Table I for the definition of the symbols (or their analogues) used here.

d. See footnote d, Table I.

TABLE III. THE PARTIAL VOLUMES OF WATER IN
AMMONIUM NITRATE SOLUTION AT 25°C COMPUTED BY
EQUATION (7)^a

x_2	v_s^b	δ^c	$(\bar{v}_1)^c$	$\Delta\bar{v}_1^c$	\bar{v}_1 Eq. (7)	\bar{v}_1^d A&G	$10^4 \Delta^c$
0.00	1.00293	0.00000	1.00293	0.00000	1.00293	1.00293	0.0
0.15	0.94433	-0.00023	1.00188	-0.00036	1.00152	1.00145	-0.7
0.30	0.88843	0.00002	0.99827	-0.00043	0.99784	0.99782	-0.2
0.375	0.86138	0.00010	0.99532	-0.00014	0.99518	0.99523	0.5
0.45	0.83489	0.00008	0.99146	0.00072	0.99218	0.99222	0.4
0.525	0.80893	-0.00015	0.98668	0.00189	0.98857	0.98868	1.1

NOTES:

a. The constants used in equations (1') and (7) are:

$$b = 0.7750, c = 0.77436, \psi_2 = 0.6652, \alpha' = (x_2/v_s) .$$

b. The data of Adams and Gibson [10].

c. Refer to the footnotes in Table I for the definition of the symbols (or their analogues) used here.

d. See footnote d, Table I.

REFERENCES

1. Glasstone, S.: *Thermodynamics for Chemists*. Van Nostrand, New York, 1947, pp. 427ff.
2. Gucker, F. T.: *J. Phys. Chem.*, vol. 38, 1934, p. 307.
3. Gibson, R. E.: *J. Phys. Chem.*, vol. 38, 1934, p. 319
4. Harned, H. S.; and Owen, B. B.: *The Physical Chemistry of Electrolytic Solutions*. Third ed., Reinhold Publ. Corp., New York, 1958, pp. 358 ff.
5. Masson, D. O.: *Phil.Mag.*, vol. 8, no. 7, 1929, p. 218.
6. Rosen, J. S.: *J. Chem. Phys.*, vol. 30, 1959, p. 547.
7. Rosen, J. S.: *J. Opt. Soc. Am.*, vol. 37, 1947, p. 932.
8. Rosen, J. S.: *J. Chem. Phys.*, vol. 17, 1949, p. 1192.
9. Rosen, J. S.: *J. Phys. Chem.*, vol. 60, 1956, p. 7.
10. Adams, L. H.; and Gibson, R. E.: *J. Am. Chem. Soc.*, vol. 54, 1932, p. 4522.

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